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Description

Emulsifier-free finely disperse systems of the oil-in-water and water-in-oil type

DEUTSCHE PATENT-AUSZEICHEN

The present invention relates to emulsifier-free finely disperse systems of the oil-in-water and water-in-oil type, preferably as cosmetic or dermatological preparations.

Emulsions are generally taken to mean heterogeneous systems which consist of two liquids which are immiscible or have only limited miscibility with one another, which are usually referred to as phases. In an emulsion, one of the two liquids is dispersed in the form of very fine droplets in the other liquid.

If the two liquids are water and oil and if oil droplets are finely dispersed in water, then this is an oil-in-water emulsion (O/W emulsion, e.g. milk). The basic character of an O/W emulsion is defined by the water. In a water-in-oil emulsion (W/O emulsion, e.g. butter), the principle is reversed, the basic character here being determined by the oil.

In order to achieve permanent dispersion of one liquid in another, emulsions in the traditional sense require the addition of an interface-active substance (emulsifier). Emulsifiers have an amphiphilic molecular structure, consisting of a polar (hydrophilic) and a nonpolar (lipophilic) molecular moiety, which are spatially separate from one another. In simple emulsions, finely disperse droplets of one phase, surrounded by an emulsifier shell, (water droplets in W/O emulsions or lipid vesicles in O/W emulsions) are present in the second phase. Emulsifiers lower the interfacial tension between the phases by positioning themselves at the interface between two liquids. At the phase boundary, they form oil/water interfacial films, which prevent irreversible coalescence of the droplets. Emulsions are frequently stabilized using emulsifier mixtures.

Traditional emulsifiers can, depending on their hydrophilic molecular moiety, be divided into ionic (anionic, cationic and amphoteric) and nonionic:

- The most well-known example of an anionic emulsifier is soap, which is usually the term used for the water-soluble sodium or potassium salts of saturated or unsaturated higher fatty acids.
- Important examples of cationic emulsifiers are quaternary ammonium compounds.
- The hydrophilic molecular moiety of nonionic emulsifiers frequently consists of glycerol, polyglycerol, sorbitans, carbohydrates and polyoxyethylene glycols, and, in most cases, is linked to the lipophilic molecular moiety via ester and ether bonds. The lipophilic molecular moiety usually consists of fatty alcohols, fatty acids or isofatty acids.

By varying the structure and the size of the polar and nonpolar molecular moiety, the lipophilicity and hydrophilicity of emulsifiers can be varied within wide limits.

A decisive factor for the stability of an emulsion is the correct choice of emulsifiers. The characteristics of all substances present in the system are to be taken into consideration here. In the case of, for example, skincare emulsions, polar oil components and, for example, UV filters lead to instability. As well as the emulsifiers, therefore, other stabilizers are also used which, for example, increase the viscosity of the emulsion and/or act as protective colloid.

Emulsions are an important type of product in the field of cosmetic and/or dermatological preparations.

Cosmetic preparations are essentially used for skin care. The main aim of skin care in the cosmetics sense is to strengthen or rebuild the skin's natural function as a barrier against environmental influences (e.g. dirt, chemicals, microorganisms) and against the loss of endogenous substances (e.g. water, natural fats, electrolytes). If this function becomes impaired, increased resorption of toxic or allergenic substances or attack by microorganisms may result, leading to toxic or allergic skin reactions.

Another aim of skin care is to compensate for the loss by the skin of lipids and water caused by daily washing. This is particularly important if the natural regeneration ability is inadequate. Furthermore, skincare products should protect against environmental influences, in particular against sun and wind, and delay skin ageing.

Cosmetic preparations are also used as deodorants. Such formulations are used to control body odour, which is produced when fresh perspiration, which is in itself odourless, is decomposed by microorganisms.

Medicinal topical compositions usually comprise one or more medicaments in an effective concentration. For the sake of simplicity, in order to distinguish clearly between cosmetic and medicinal use and corresponding products, reference is made to the legal provisions in the Federal Republic of Germany (e.g. Cosmetics Directive, Foods and Drugs Act).

The use of customary emulsifiers in cosmetic or dermatological preparations is in itself acceptable. Nevertheless, emulsifiers, like ultimately any chemical substance, may in certain circumstances cause allergic reactions or reactions based on oversensitivity of the user.

For example, it is known that certain light dermatoses are triggered by certain emulsifiers, but also by various fats and simultaneous exposure to sunlight. Such light dermatoses are also called "Mallorca acne". There has thus been no lack of attempts to reduce the amount of customary emulsifiers to a minimum, in the ideal case even to zero.

A reduction in the required amount of emulsifier can, for example, be achieved by taking advantage of the fact that very finely divided solid particles have an additional stabilizing action. The solid substance accumulates at the oil/water phase boundary in the form of a layer, as a result of which coalescence of the disperse phases is prevented. It is not the chemical properties of the solid particles which are of fundamental importance here, but the surface properties.

Around 1910, Pickering prepared paraffin/water emulsions which were stabilized merely by the addition of various solids, such as basic copper sulphate, basic iron sulphate or other metal sulphates. This type of emulsion is thus also referred to as a Pickering emulsion.

The original forms of Pickering emulsions initially surfaced, as it were, as undesired secondary effects in a variety of industrial processes, such as, for example, in secondary oil recovery, the extraction of bitumen from tar sand and other separation processes involving

two immiscible liquids and fine, dispersed solid particles. These are generally W/O emulsions which are stabilized by mineral solids. Accordingly, investigation of corresponding systems, such as, for example, the oil/water/soot or oil/water/slant dust systems was initially the focus of research activity.

Basic experiments have shown that one characteristic of a Pickering emulsion is that the solid particles are arranged at the interface between the two liquid phases, where they form, as it were, a mechanical barrier against the combining of the liquid droplets.

It is a relatively new technical development to use Pickering emulsions as a base for cosmetic or dermatological preparations.

One way of achieving solids stabilization in the sense of a pickering emulsion in a cosmetic or dermatological preparation is, according to May-Alert (*Pharmazie in unserer Zeit [Pharmacy in our time]*, Vol. 15, 1986, No. 1, 1-7) for example, to use emulsifier mixtures which comprise both anionic and cationic surfactants. Since mixing anionic and cationic surfactants always results in the precipitation of insoluble, electroneutral compounds, deliberate precipitation of these neutral surfactants in the oil/water interface makes it possible to achieve additional solids stabilization.

European Laid-open Specification 0 686 391, moreover, describes emulsions of the water-in-oil type which are free from surface-active substances and are stabilized only by solids. Stabilization is achieved here using spherical polyalkylsilsesquioxane particles which have a diameter of from 100 nm up to 20 µm. These emulsions can be referred to as Pickering emulsions according to that mentioned above.

Pickering emulsions are stabilized by the use of suitable solids or pigments. However, the preparations of the prior art generally have the disadvantage that they are limited to a narrow field of application or a restricted choice of starting materials since they can only be stably formulated in this manner. For many areas of cosmetics (e.g. for the field of face care), Pickering emulsions of the prior art have unsatisfactory cosmetic properties.

The object was therefore to remedy the disadvantages of the prior art. In particular, the intention was to provide cosmetic and dermatological bases for cosmetic and dermatological preparations which are characterized by good skin tolerability.

In addition, an object of the present invention was to provide products with the widest possible variety of applications. For example, the intention was to provide bases for preparation forms such as cleansing emulsions, facecare and bodycare preparations or deodorants, but also distinctly medicinal-pharmaceutical presentations, for example preparations against acne and other skin conditions.

It was surprising and in no way predictable by the person skilled in the art that Pickering emulsions, which are finely disperse systems of the water-in-oil or oil-in-water type, comprising

- (1) an oil phase which contains at least one wax and/or one oil thickener,
- (2) a water phase,
- (3) at least one type of microfine particles which
  - a) have an average particle size of less than 200 nm, which
  - b) display both hydrophilic and lipophilic properties, i.e. which have amphiphilic character, and are dispersible both in water and in oil and which
  - c) have optionally been coated on the surface and
- (4) at most 0.5% by weight of one or more emulsifiers,  
overcome the disadvantages of the prior art.

According to the invention, it is particularly advantageous if the preparations comprise significantly less than 0.5% by weight of one or more emulsifiers or are even entirely free from emulsifiers.

The preparations according to the invention are extremely satisfactory preparations in every respect which have considerably higher stability compared with traditional Pickering emulsions and are therefore suitable in particular to serve as bases for preparation forms having diverse application purposes. In particular, W/O Pickering emulsions within the meaning of the present invention are, surprisingly, markedly stable.

In addition, the preparations according to the invention are characterized by excellent skin tolerability. In addition, it was surprising that preparations according to the invention, which are in the form of a sunscreen, exhibit higher effectiveness than customary sunscreen formulations.

While preparations of the prior art having a pigment content of as little as 1% by weight produce a dull feel following their application to the skin, which increases further with higher pigment concentrations, the preparations according to the invention, surprisingly, do not leave a dry or dull impression on the skin, but on the contrary exhibit excellent cosmetic properties.

Although the prior art recognizes, in addition to Pickering emulsions, emulsifier-free, finely disperse cosmetic or dermatological preparations, which are generally referred to as hydrodispersions and which are dispersions of a liquid, semisolid or solid inner (discontinuous) lipid phase in an outer aqueous (continuous) phase, the prior art was unable to point the way to the present invention.

In hydrodispersions of a liquid lipid phase in an external aqueous phase, the stability can be guaranteed, for example, by building up a gel structure in the aqueous phase in which the lipid droplets are stably suspended.

German Laid-Open Specification 44 25 268 describes stable finely dispersed, emulsifier-free cosmetic or dermatological preparations of the oil-in-water type which, in addition to an oil and a water phase, contain one or more thickeners from the group consisting of the acrylic acid polymers, polysaccharides and their alkyl ethers, where for these thickeners a lowering of interfacial tension must not be measurable.

Based on similar hydrodispersions, German Laid-Open Specification 43 03 983 discloses cosmetic or dermatological sunscreen formulations which are essentially free of emulsifiers, inorganic micropigments which serve as UV filter substances being incorporated into the lipid phase of the hydrodispersion.

O/W Pickering emulsions within the meaning of the present invention, however, are obtainable by first dispersing amphilic particles according to the invention, which are

suitable for the preparation of O/W Pickering emulsions, in the aqueous phase and then combining the aqueous phase with the fatty phase. W/O Pickering emulsions according to the invention, however, are obtainable by dispersing amphiphilic particles which are suitable for the preparation of W/O Pickering emulsions in the fatty phase.

Waxes:

According to the stipulation of the German Society for Fat Economic (*Fette, Seifen, Anstrichmittel*, 76, 135 [1974]), as a rule the mechanicophysical properties of the waxes, which are decisive for their use, are used for the characterization of the term "wax", while the respective chemical composition remains unconsidered in the determination of the term.

"Wax" is - similarly to "resin" - a collective description of a number of natural or synthetically obtained substances, which as a rule have the following properties: kneadable at 20°C, solid to friably hard, coarse- to fine-crystalline, transparent to opaque, but not glassy, melting above 40°C without decomposition, even slightly above the melting point of comparatively low viscosity and non-thread-drawing, strongly temperature-dependent consistency and tolerability and polishable under slight pressure. In borderline cases, if more than one of the abovementioned properties is not fulfilled in a substance, it is not a wax within the meaning of this definition. Waxes differ from similar synthetic or natural products (e.g. resins, plastic materials etc.) mainly in that as a rule they turn into the molten, low-viscosity state approximately between 50 and 90°C, in exceptional cases also up to approximately 200°C, and are virtually free of ash-forming compounds.

Oil thickeners are substances which, for example, are capable of absorbing liquid oils with formation of homogeneous, viscous and colloidal solutions. They are added to cosmetic or dermatological preparations during their preparation or processing in order to thicken the fatty phase.

Waxes and/or oil thickeners within the meaning of the present invention are compounds which are characterized in that, together with the other oil components of the preparations according to the invention (such as, for example, polar, liquid compounds,

UV filters and their solvents etc.), they form a material which is pasty (viscous) and spreadable at room temperature, which has a viscosity of more than 5000 mPa·s at 20°C.

Those advantageous according to the invention are, for example, natural waxes of animal and vegetable origin, such as, for example, beeswax, China wax, bumblebee wax and other insect waxes, in particular those mentioned below.

Beeswax, for example, is a secretion product from glands of honeybees, which they use for building honeycombs. Yellow (*Cera flava*), brown or red so-called raw wax is obtainable, for example, by melting the combs freed from the honey by centrifuging, separating the melt from solid impurities and allowing the raw wax thus obtained to solidify. The raw wax can be bleached completely white (*Cera alba*) by treatment with oxidizing agents.

Beeswax consists of the readily alcohol-soluble cerin, a mixture of cerotic acid  $\text{CH}_3(\text{CH}_2)_{24}\text{COOH}$  and melissic acid  $\text{CH}_3(\text{CH}_2)_{28}\text{COOH}$  and of an ester mixture called myricin consisting of about 70 esters of  $\text{C}_{16}$ - to  $\text{C}_{36}$ -acids and  $\text{C}_{24}$ - to  $\text{C}_{36}$ -alcohols. Essential constituents of beeswax are myricyl palmitate, myricyl cerotate and paraffin.

Other insect waxes such as, for example, bumblebee wax, shellac wax or China wax are essentially mixtures of various esters. China wax, for example, is deposited or produced in China and Japan from the Chinese wax scale (*Coccus ceriferus*) living on the Chinese ash and the scale species *Ceroplastes ceriferus* and *Ericerus pela*. It is scraped from the trees and purified by remelting in boiling water. The main constituent of China wax is the cerotic acid ester of ceryl alcohol.

Shellac wax is obtained from lac, the secretion of the female lac insects (*Kerria lacca*), which live in huge colonies (lac is derived from the Hindi word "Lakh" for 100,000) on trees and shrubs in Southern Asia (India, Burma, Southern China). The shellac wax accessible by solvent extraction contains myricyl alcohol, melissic acid and other wax alcohols and acids or their esters as essential constituents.

Plant waxes are also advantageous within the meaning of the present invention. Those which can preferably be used are cuticular waxes of lower and higher plants, algae, lichens, mosses and fungi, such as, for example, candelilla wax, carnauba wax, Japan wax, esparto grass wax, cork wax, rice wax, sugar cane wax, fruit waxes, e.g. apple wax, flower waxes, leaf waxes from conifers, coffee wax, flax wax, sesame wax, jojoba oil and such like.

Candelilla waxes, for example, are brownish to yellowish brown, hard waxy materials which are soluble in lipophilic solvents. Candelilla wax contains odd-number aliphatic hydrocarbons (about 42%), esters (about 39%), wax acids and wax alcohols. It can be obtained, for example, from the comminuted, fleshy leaves of a thornless spurge species (*Euphorbia cerifera*) by boiling with aqueous sulphuric acid.

Carnauba wax is a yellowish, greenish or dark-grey material which can be obtained in various qualities, obtained by selection from the leaves of the Brazil fan palm *Copernicia prunifera* or carnauba palm (*Carnauba cerifera*) by, for example, brushing the wax dust from the withered fronds, melting it and filtering it and, after solidification, breaking it into pieces. Carnauba wax can be lightened by bleaching. It contains about 85% of esters, in each case approximately 2-3% of free wax acids (carnaubic, behenic, lignoceric, melissic and cerotinic acid), long-chain alcohols, diols and saturated hydrocarbons.

Japan wax (also: *Cera japonica*) is colourless or yellowish, pure plant fat, which can be obtained, for example, in Japan from the fruits of a tree-like sumac plant (*Rhus succedanea*) by boiling. The main constituents of Japan wax are glyceryl palmitate and esters of japonic acid (heneicosanedioic acid,  $C_{21}H_{40}O_4$ ), phellogenic acid (docosanedioic acid,  $C_{22}H_{42}O_4$ ) and of tricosanedioic acid ( $C_{23}H_{44}O_4$ ).

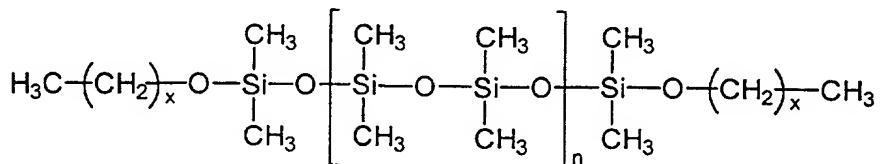
Esparto wax is obtained as a by-product in pulp and paper manufacture from the esparto grass (Graminaceae) indigenous to Mediterranean countries. It consists to about 15 to 17% of wax acids (e.g. cerotic and melissic acid), to 20 to 22% of alcohols and hydrocarbons and to 63 to 65% of esters.

Particularly advantageous natural waxes within the meaning of the present invention are those obtained, for example, under the tradenames *Permulgın 1550* and *Permulgın*

4002 from KOSTER KEUNEN and those obtainable under the tradenames Schellack Wachs 7302 L and Candellila Wachs 2039 L from the KAHL wax refinery.

Chemically modified waxes and synthetic waxes are furthermore advantageous according to the invention. Preferred modified waxes are, for example, beeswax esters, in particular the alkyl beeswaxes obtainable from KOSTER KEUNEN under the tradenames BW Ester BW 67, BW Ester BW 80.

Preferred synthetic waxes are, for example, that obtainable under the tradename beeswax component B 85 from SCHLICKUM and silicone-based waxes, such as, for example, dialkoxydimethylpolysiloxanes, which are distinguished by the following structure



in which x is a number between 18 and 24. Behenoxy dimethicone, for which x from the above structural formula is 21 and which is obtainable under the tradename Abil® Wax 2440 from Th. Goldschmidt AG is particularly advantageous. A silicone-based wax, which is obtainable under the tradename Siliconyl Beeswax from KOSTER KEUNEN is furthermore preferred according to the invention.

Further advantageous synthetic waxes are certain fatty acids and/or fatty acid mixtures, for example C<sub>16-36</sub>-fatty acids, in particular those which are obtainable under the tradename Syncrowax AW1C from Croda GmbH.

Ester waxes which are esters of

1. a saturated and/or unsaturated, branched and/or unbranched mono- and/or dicarboxylic acid having 12 to 40 carbon atoms and
2. a saturated and/or unsaturated, branched and/or unbranched alcohol having 12 to 40 carbon atoms

are moreover advantageous within the meaning of the present invention.

Ester waxes which are selected from the group listed below are particularly advantageous:

<b>Ester wax</b>	<b>Tradename</b>	<b>Obtainable from</b>
Myristyl myristate	Cetiol MM	Henkel KGaA
Cetyl palmitate	Cutina CP	Henkel KGaA
C <sub>14-34</sub> alkyl stearate	Kesterwachs K 76 H	KOSTER KEUNEN
C <sub>20-40</sub> dialkyl dimerate	Kesterwachs K 80 D	KOSTER KEUNEN
Ditetrasanyl dimerate	Kesterwachs K70D	KOSTER KEUNEN
C <sub>16-38</sub> alkyl hydroxystearoyl stearate	Kesterwachs K80P	KOSTER KEUNEN
C <sub>20-40</sub> alkyl stearoyl stearoyl stearate	Kesterwachs K80P-VS	KOSTER KEUNEN
C <sub>20-40</sub> alkyl stearate	Kesterwachs K 82	KOSTER KEUNEN
Hydroxystearyl hydroxystearate	Elfacos C26	AKZO NOBEL

ESTERS OF GLYCOL  
Esters of glycol, in particular glycol esters of lignoceric acid ( $\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$ ), of cerotic acid ( $\text{CH}_3(\text{CH}_2)_{24}\text{COOH}$ ) and/or of montanic acid ( $\text{CH}_3(\text{CH}_2)_{26}\text{COOH}$ ) are furthermore advantageous. Glycol esters of montanic acid ( $\text{CH}_3(\text{CH}_2)_{26}\text{COOH}$ ) are very particularly advantageous within the meaning of the present invention. An advantageous glycol montanate is obtainable, for example, in a mixture with a butylene glycol montanate under the tradename Wax E Pharma from Clariant.

It is furthermore advantageous to select the wax components from the group consisting of the glycerides, in particular from the group consisting of the triglycerides. The glycerides and triglycerides listed below are particularly advantageous:

<b>Glyceride</b>	<b>Tradename</b>	<b>Obtainable from</b>
C <sub>16-18</sub> triglyceride	Cremeol HF-52-SPC	Aarhus Oliefabrik
Glyceryl hydroxystearate	Naturchem GMHS	Rahn
Hydrogenated cocoa glycerides	Softisan 100	Hüls AG
Caprylic/capric/isostearic/adipic triglyceride	Softisan 649	Dynamit Nobel
C <sub>18-36</sub> triglyceride	Syncrowax HGLC	Croda GmbH
Glyceryl tribehenate	Syncrowax HRC	Croda GmbH
Glyceryl tri(12-hydroxystearate)	Thixicin R	Rheox/NRC
Hydrogenated castor oil	Cutina HR	Henlek KGaA
C <sub>16-24</sub> triglyceride	Cremeol HF-62-SPC	Aarhus Oliefabrik

Shea butter, also called karité oil or galam butter (CAS No. 68920-03-6), is also particularly preferred. Shea butter is the fat of the seeds or kernels of the plant *Butyrospermum Parkii* belonging to the family of the Sapotaceae, which consists to approximately 34 to 45% by weight of solid fatty acids (principally stearic acid) and to approximately 50 to 60% by weight of liquid fatty acids (principally comprising oleic acid).

According to the invention, the waxes are furthermore preferably selected from the group consisting of the saturated and/or unsaturated, branched and/or unbranched fatty alcohols having 14 to 40 carbon atoms; behenyl alcohol ( $C_{22}H_{45}OH$ ), cetearyl alcohol [a mixture of cetyl alcohol ( $C_{16}H_{33}OH$ ) and stearyl alcohol ( $C_{18}H_{37}OH$ )], cetyl arachidol [2-hexadecyl-1-eicosanol ( $C_{36}H_{73}OH$ )], and/or 2-tetradecyloctadecanol ( $C_{32}H_{65}OH$ ) are particularly preferred. Advantageous embodiments of the two last-mentioned fatty alcohols are obtainable from Condea under the tradenames Isofol 36 and Isofol 32.

Within the meaning of the present invention, oil thickeners are selected, for example, from the group consisting of the metal soaps. Metal soaps are the salts of higher fatty acids, resin acids and naphthenic acids (stearates, palmitates, oleates, linoleates, resinate, laurates, octanoates, ricinoleates, 12-hydroxystearates, naphthenates, tallates and the like) with the exception of the sodium and potassium salts, that is, for example, the salts of the metals aluminium, barium, calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, nickel, lead, tin, strontium and zinc.

Of course, the person skilled in the art knows that among the metal soaps are some which would be fundamentally suitable for the realization of the present invention, but which should nevertheless be dispensed with because of harmful action on the skin or other concomitant factors. According to the CIR panel, a committee which checks whether adequate toxicity data are available for substances which are employed in the cosmetic industry (CIR: Cosmetic Ingredient Review), for example, lithium, aluminium, calcium and zinc stearates are to be regarded as harmless in the doses which are customarily used for the preparation of cosmetic compositions. In addition to the requirements of various pharmaceutical regulations, magnesium stearate also meets the demands which foodstuffs quality sets.

For the sake of simplicity, reference is made to the relevant regulations for unambiguous differentiation between cosmetically harmful and harmless substances (e.g. Cosmetics decree, Food and Drugs Act, official pharmacopoeia, publications of the CIR panel etc.).

Aluminium stearate and magnesium stearate are particularly preferred within the meaning of the present invention.

The oil thickener(s) selected from the group consisting of the layered silicates, in particular from the group consisting of the bentonites and hectorites, is/are furthermore advantageous. Bentonites are clays and rocks which contain smectites, especially montmorillonite, as the main minerals. Modified bentonites and hectorites, for example those whose organophilicity has been increased by reaction with quaternary ammonium compounds, are particularly preferred within the meaning of the present invention. These types of bentonites are also designated as organophilic bentonites or alternatively bentones. Those which are very particularly preferred are stearalkonium hectorite, a reaction product of hectorite and stearalkonium chloride (benzyldimethylstearylammmonium chloride), and quaternium-18 hectorite, a reaction product of hectorite and a quaternary ammonium salt, which are obtainable from Nordmann & Rassmann, for example, under the tradenames Bentone 27 and Bentone 38.

The total amount of one or more waxes and/or oil thickeners in the finished cosmetic or dermatological preparations is advantageously chosen to be in the range of 0.5 to 20.0% by weight, preferably between 1.0 and 5.0% by weight, based on the total weight of the preparations.

It is also advantageous, although not obligatory, for the Pickering emulsions according to the invention to comprise other auxiliaries which can contribute to reducing or preventing a dull or dry feel on the skin following their application, where it is possible that the main purpose of these substances is a different one. Preferably, these substances are, for example, chosen from the group of unsymmetrically substituted s-triazine derivatives, cyclodextrins, film formers and polymeric moisturizers, it being possible for these substances to be present either individually or in a mixture.

The cosmetic properties of the Pickering emulsions according to the invention can additionally, for example, be further improved by also using oils in the oil phase which have a viscosity of less than 30 mPa.s, in particular of less than 20 mPa.s (determined using a rheometer from Contraves (Rheomat 108E) at a shear gradient of 500/s and a temperature of 25°C).

**Microfine particles:**

The amphiphilic character of the microfine particles according to the invention is evident, for example, from the fact that they are dispersible both in water and in oil.

It is advantageous to choose the average particle diameter of the particles used to be between 1 nm and 200 nm, particularly advantageously between 5 nm and 100 nm.

It is also advantageous to choose the concentration of all amphiphilic particles according to the invention to be greater than 0.1% by weight, particularly advantageously between 0.1% by weight and 30% by weight, based on the total weight of the preparations.

For the purposes of the present invention, advantageous particles are all those which are suitable for stabilizing Pickering W/O emulsions or Pickering O/W emulsions. It is essentially insignificant for the present invention in which of the potentially naturally occurring modifications the particles are present.

To stabilize the Pickering emulsions, preference is given to using untreated, virtually pure pigment particles, in particular those which can be used as dyes in the food industry and/or as absorbers of UV radiation in sunscreens. Examples of advantageous pigments are the zinc oxide pigments available from Merck which are available under the tradenames Zinkoxid neutral from Haarmann & Reimer or NanoX from Harcros Chemical Group.

For the purposes of the present invention, Pickering emulsions are likewise advantageously stabilized by inorganic pigments which have been surface-treated ("coated") to repel water, where at the same time the intention is to form or retain the

amphiphilic character. This surface-treatment can consist in providing the pigments with a thin hydrophobic layer by processes known per se.

One such process, which is described below using titanium dioxide as an example, consists in, for example, producing the hydrophobic surface layer according to the following reaction



n and m are arbitrary stoichiometric parameters, and R and R' are the desired organic radicals. Particularly advantageous are  $\text{TiO}_2$  pigments, for example those coated with aluminium stearate, available under the tradename MT 100 T from TAYCA.

A further advantageous coating of the inorganic pigments consists of dimethylpolysiloxane (also: dimethicone), a mixture of completely methylated, linear siloxane polymers which are terminally blocked with trimethylsiloxy units. For the purposes of the present invention, particularly advantageous pigments are zinc oxide pigments which are coated in this way.

Also advantageous is a coating of the inorganic pigments with a mixture of dimethylpolysiloxane, in particular dimethylpolysiloxane having an average chain length of from 200 to 350 dimethylsiloxane units, and silica gel, which is also referred to as simethicone. It is particularly advantageous if the inorganic pigments have been additionally coated with aluminium hydroxide or hydrated aluminium oxide (also: alumina, CAS No.: 1333-84-2). Particularly advantageous are titanium dioxides which have been coated with simethicone and alumina, it being possible for the coating to also comprise water. One example thereof is the titanium dioxide available under the tradename Eusolex T2000 from Merck.

For the purposes of the present invention it is also advantageous to use a mixture of different pigment types either within a crystal, for example as mixed iron oxide, or by combination of two or more pigment types within a preparation.

The Pickering emulsions are also preferably stabilized by boron nitride particles, for example by the boron nitrides listed below:

Tradename	Available from
Boron Nitride Powder	Advanced Ceramics
Boron Nitride Powder	Sintec Keramik
Ceram Blanche	Kawasaki
HCST Boron Nitride	Stark
Très BN®	Carborundum
Wacker-Bornitrid BNP	Wacker-Chemie

It is advantageous to choose the average particle diameter of the boron nitride particles used to be less than 20 µm, particularly advantageously less than 15 µm.

For the purposes of the present invention, Pickering emulsions are likewise advantageously stabilized by boron nitride particles which have been surface-treated ("coated") to repel water, where at the same time the intention is to form or retain the amphiphilic character.

An advantageous coating of the boron nitride particles consists of dimethylpolysiloxane (dimethicone). The boron nitride particles treated with dimethicone and available from Carborundum under the tradename Très BN® UHP 1106 are advantageous, for example.

Also advantageous is a coating of the boron nitride particles with polymethylhydrogensiloxane, a linear polysiloxane which is also referred to as methicone. Advantageous boron nitride particles treated with methicone are, for example, those available from Carborundum under the tradename Très BN® UHP 1107.

It is also advantageous to stabilize the Pickering emulsions according to the invention using microfine polymer particles.

For the purposes of the present invention, examples of advantageous microfine polymer particles are polycarbonates, polyethers, polyethylenes, polypropylenes, polyvinyl chloride, polystyrene, polyamides, polyacrylates and the like.

Advantageous according to the invention are, for example, microfine polyamide particles which are available under the tradename SP-500 from TORAY. Also advantageous are polyamide 6 (also: nylon 6) and polyamide 12 (also: nylon 12) particles. Polyamide 6 is the polyamide formed from  $\epsilon$ -aminocaproic acid (6-aminohexanoic acid) or  $\epsilon$ -caprolactam [poly( $\epsilon$ -caprolactam)], and polyamide 12 is a poly( $\epsilon$ -laurolactam) from  $\epsilon$ -laurolactam. For the purposes of the present invention, Orgasol<sup>®</sup> 1002 (polyamide 6) and Orgasol<sup>®</sup> 2002 (polyamide 12) from ELF ATOCHEM, for example, are advantageous.

Other advantageous polymer particles are microfine polymethacrylates. Such particles are available, for example, under the tradename POLYTRAP<sup>®</sup> from DOW CHEMICAL.

It is particularly advantageous, but not obligatory, if the microfine polymer particles used have been surface-coated. This surface-treatment can consist in providing the pigments with a thin hydrophilic layer by processes known per se. Advantageous coatings consist, for example, of TiO<sub>2</sub>, ZrO<sub>2</sub> or also other polymers, such as, for example, polymethyl methacrylate.

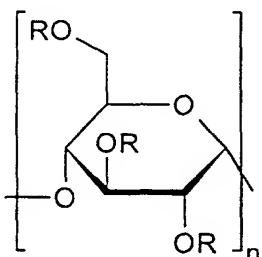
Particularly advantageous microfine polymer particles for the purposes of the present invention are also obtainable by the process, described in US Patent Specification 4,898,913, for the hydrophilic coating of hydrophobic polymer particles.

It is advantageous to choose the average particle diameter of the microfine polymer particles used to be less than 100  $\mu\text{m}$ , particularly advantageously less than 50  $\mu\text{m}$ . In this connection, it is essentially insignificant in which form (platelets, rods, spherules, etc.) the polymer particles used are present.

In addition, it is advantageous to stabilize the Pickering emulsions according to the invention using modified polysaccharides.

For the purposes of the present invention, modified polysaccharides are, for example, obtainable by reaction of starch with mono-, bi- or polyfunctional reagents or oxidizing agents in reactions which proceed in a largely polymer-analogous manner.

Such reactions are based essentially on modifications of the hydroxyl groups of the polyglucans by etherification, esterification or selective oxidation. This produces, for example, so-called starch ethers and starch esters of the general structural formula

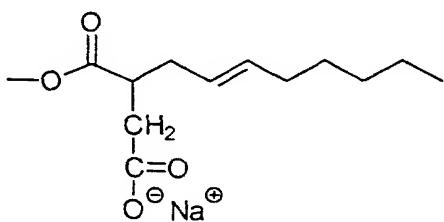


## Structural formula (I)

in which R can, for example, be a hydrogen and/or an alkyl and/or an aralkyl radical (in the case of starch ethers) or a hydrogen and/or an organic and/or inorganic acid radical (in the case of starch esters). Starch ethers and starch esters are advantageous, modified polysaccharides for the purposes of the present invention.

Particularly advantageous starch ethers are, for example, those which are obtainable by etherification of starch with tetramethylolacetylenediurea and which are referred to as non-mucilaginous starch (nonswelling starch).

Also particularly advantageous are starch esters and salts thereof, for example the sodium and/or aluminium salts of half-esters of starch which have low degrees of substitution, in particular sodium starch n-octenyl succinate of the structural formula (II) in which R is characterized by the following structure



and which is available, for example, under the tradename Amiogum® 23 from CERESTAR, and aluminium starch octenyl succinates, in particular those available under the tradenames Dry Flo® Elite LL and Dry Flo® PC from CERESTAR.

It is advantageous to choose the average particle diameter of the modified polysaccharide used to be less than 20 µm, particularly advantageously less than 15 µm.

The list of given modified polysaccharides which are able to stabilize Pickering emulsions according to the invention is of course not intended to be limiting. For the purposes of the present invention, modified polysaccharides are obtainable in a large number of ways known per se, both of a chemical and a physical nature.

The abovementioned amphiphilic particles are outstandingly suitable both for the stabilization of W/O Pickering emulsions and for the stabilization of O/W Pickering emulsions. Microfine particles according to the invention are mentioned below which advantageously in particular stabilize one of the two emulsion types W/O or O/W.

#### W/O Pickering emulsions:

The water phase proportion in the W/O Pickering emulsions according to the invention is preferably selected from the range of 0.5 to 75% by weight, based on the total weight of the formulations.

Magnesium silicates (also: talc), for example those obtainable under the tradename Talkum Micron from Grolmann, in particular are also advantageous for the stabilization of W/O Pickering emulsions.

#### O/W Pickering emulsions:

The fatty phase fraction of the O/W Pickering emulsions according to the invention is preferably selected from the range of 0.5 to 75% by weight, based on the total weight of the formulations.

Untreated, almost pure pigment particles, for example titanium dioxide pigments, in particular those which are obtainable under the tradename KRONOS® 1171 ( $TiO_2$ ) from Kronos Titan are also particularly advantageous for the stabilization of O/W Pickering emulsions within the meaning of the present invention.

O/W Pickering emulsions within the meaning of the present invention are furthermore particularly advantageously stabilized by metal oxide particles which are coated with aluminium hydroxide and/or silicon dioxide. Advantageous embodiments are, for example, titanium dioxide particles, which are obtainable under the name EUSOLEX® TA from Merck.

It is furthermore advantageous, although not obligatory, to combine the microfine particles according to the invention with further amphiphilic particles which can optionally also contribute to the stabilization of the Pickering emulsions.

Such particles are, for example, titanium dioxide pigments which are coated with octylsilanol, and/or silicon dioxide particles which have a water-repellent treatment on the surface. Suitable silicon dioxide particles are, for example, spherical polyalkylsilsesquioxane particles, such as are mentioned in European Laid-Open Specification 0 686 391. Such polyalkylsilsesquioxane particles are obtainable, for example, from Degussa under the tradenames Aerosil R972 and Aerosil 200V. Suitable titanium dioxide particles are likewise obtainable from Degussa under the tradename T805.

The Pickering emulsions according to the invention can serve as a base for cosmetic or dermatological formulations. These can be combined in the customary manner and serve, for example, for the treatment and care of the skin, as a lipcare product, as a deodorant product and as a make-up or make-up removal product in decorative cosmetics or as a sunscreen preparation. For use, the cosmetic and dermatological preparations according to the invention are applied to the skin in adequate amount in the manner customary for cosmetics.

Accordingly, cosmetic or topical dermatological compositions within the meaning of the present invention, depending on their make-up, can be used, for example, as a skin-protection cream, cleansing milk, sunscreen lotion, nutrient cream, day cream or night cream, etc. It is optionally possible and advantageous to use the compositions according to the invention as a base for pharmaceutical formulations.

The cosmetic and dermatological preparations according to the invention can contain cosmetic auxiliaries, such as are customarily used in such preparations, e.g. preservatives, bactericides, perfumes, substances for preventing foaming, colorants, pigments which have a colouring action, thickening agents, emollient, moisturizing and/or humectant substances, fats, oils, waxes or other customary constituents of a cosmetic or dermatological formulation such as alcohols, polyols, polymers, foam stabilizers, electrolytes, organic solvents or silicone derivatives.

Pickering emulsions according to the invention can also contain thickening agents in order to improve the tactile properties of the emulsion.

In particular, the Pickering emulsions according to the invention can also contain antioxidants. According to the invention, favourable antioxidants which can be used are all antioxidants suitable or customary for cosmetic and/or dermatological applications.

Advantageously, the antioxidants are selected from the group consisting of amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and their derivatives, imidazoles (e.g. urocanic acid) and their derivatives, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and their derivatives (e.g. anserine), carotenoids, carotenes (e.g.  $\alpha$ -carotene,  $\beta$ -carotene, lycopene) and their derivatives, chlorogenic acid and its derivatives, lipoic acid and its derivatives (e.g. dihydrolipoic acid), aurothioglucose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and their glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl,  $\gamma$ -linoleyl, cholesteryl and glyceryl esters) and their salts, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and its derivatives (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulphoximine compounds (e.g. buthionine sulphoximine, homocysteine sulphoximine, buthionine sulphone, penta-, hexa- and heptathionine sulphoximine) in very small tolerable doses (e.g. pmol to  $\mu$ mol/kg), furthermore (metal) chelators (e.g.  $\alpha$ -hydroxy fatty acids, palmitic acid, phytic acid, lactoferrin),  $\alpha$ -hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and their derivatives, unsaturated fatty acids and their derivatives (e.g.  $\gamma$ -linolenic acid, linoleic acid, oleic acid), folic acid and its derivatives, ubiquinone and ubiquinol and their derivatives, vitamin C and derivatives (e.g. ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives

(vitamin A palmitate) and coniferyl benzoate of benzoin, rutic acid and its derivatives,  $\alpha$ -glycosylrutin, ferulic acid, furfurylideneoglucitol, carnosine, butylhydroxytoluene, butylhydroxyanisole, nordihydroguaiac acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and its derivatives, mannose and its derivatives, zinc and its derivatives (e.g. ZnO, ZnSO<sub>4</sub>), selenium and its derivatives (e.g. selenomethionine), stilbenes and their derivatives (e.g. stilbene oxide, trans-stilbene oxide), and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of these said active compounds.

The amount of the abovementioned antioxidants (one or more compounds) in the preparations according to the invention is preferably from 0.001 to 30% by weight, particularly preferably from 0.05 - 20% by weight, in particular 1 - 10% by weight, based on the total weight of the preparation.

If vitamin E and/or its derivatives are the antioxidant(s), it is advantageous to select their respective concentrations from the range of 0.001 - 10% by weight, based on the total weight of the formulation.

If vitamin A, or vitamin A derivatives, or carotenes or their derivatives are the antioxidant(s), it is advantageous to select their respective concentrations from the range of 0.001 - 10% by weight, based on the total weight of the formulation.

Cosmetic and dermatological preparations which are present in the form of a sunscreen composition are also favourable. These preferably contain at least one UV-A filter substance and/or at least one UV-B filter substance and/or at least one further inorganic pigment from the group consisting of the oxides of iron, zirconium, silicon, manganese, aluminium, cerium and mixtures thereof and also modifications in which the oxides are the active agents.

However, it is also advantageous within the meaning of the present invention to make available those cosmetic and dermatological preparations whose main purpose is not protection from sunlight, but which nevertheless contain substances which protect against UV. Thus, UV-A and UV-B filter substances are usually incorporated, for example, into day creams.

Advantageously, preparations according to the invention can contain substances which absorb UV radiation in the UV-B range, the total amount of filter substances being, for example, 0.1% by weight to 30% by weight, preferably from 0.5 to 10% by weight, in particular 1.0 to 6.0% by weight, based on the total weight of the preparations, in order to make available cosmetic preparations which protect the hair or the skin from the entire range of ultraviolet radiation.

If the emulsions according to the invention contain UV-B filter substances, these can be oil-soluble or water-soluble. Oil-soluble UV-B filters which are advantageous according to the invention are, for example:

- 3-benzylidene camphor derivatives, preferably 3-(4-methylbenzylidene)camphor, 3-benzylidene camphor;
- 4-aminobenzoic acid derivatives, preferably 2-ethylhexyl 4-dimethylaminobenzoate, amyl 4-dimethylaminobenzoate;
- esters of cinnamic acid, preferably 2-ethylhexyl 4-methoxycinnamate, isopentyl 4-methoxycinnamate;
- esters of salicylic acid, preferably 2-ethylhexyl salicylate, 4-isopropylbenzyl salicylate, homomenthyl salicylate,
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- esters of benzalmalonic acid, preferably di(2-ethylhexyl) 4-methoxybenzalmalonate,
- triazine derivatives which are symmetrical with respect to the C<sub>3</sub> axis of the triazine parent structure, preferably tris(2-ethylhexyl) 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)trisbenzoate,
- benzotriazole derivatives, preferably 2,2'-methylenebis(6-(2H-benzotriazole-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol)
- and UV filters bonded to polymers.

Advantageous water-soluble UV-B filters are, for example:

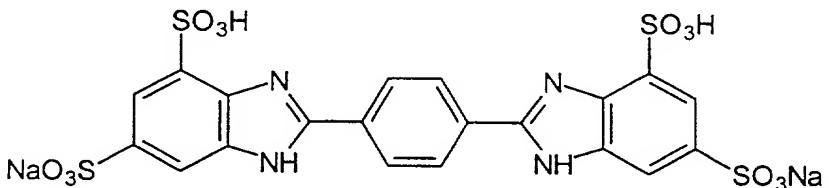
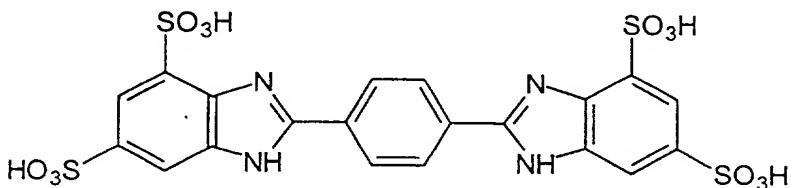
- salts of 2-phenylbenzimidazole-5-sulphonic acid such as its sodium, potassium or its triethanolammonium salt, and the sulphonic acid itself;
- sulphonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid and its salts;

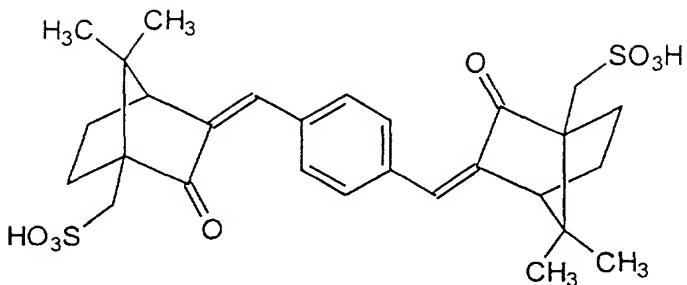
- sulphonic acid derivatives of 3-benzylidene camphor, such as, for example, 4-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid, 2-methyl-5-(2-oxo-3-bornylidenemethyl)sulphonic acid and its salts.

The list of the UV-B filters mentioned, which can be used in the Pickering emulsions according to the invention, should, of course, be non-limiting.

It can also be advantageous in Pickering emulsions according to the invention to use UV-A filters which have hitherto been customarily contained in cosmetic preparations. These substances are preferably derivatives of dibenzoylmethane, in particular 1-(4'-tert-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dione and 1-phenyl-3-(4'-isopropylphenyl)propane-1,3-dione.

Other advantageous UV-A filter substances are phenylene-1,4-bis(2-benzimidazyl)-3,3'-5,5'-tetrasulphonic acid:





Preparations which contain UV-A filters are also a subject of the invention. The amounts used for the UV-B combination can be employed.

Preparations according to the invention can also be advantageously used as bases for cosmetic deodorants and antiperspirants, so that a particular embodiment of the present invention relates to Pickering emulsions as bases for cosmetic deodorants.

Cosmetic deodorants are used to control body odour which arises when fresh perspiration, which is in itself odourless, is decomposed by microorganisms. Customary cosmetic deodorants are based on various modes of action.

In antiperspirants, astringents, mainly aluminium salts, such as aluminium hydroxychloride (aluminium chlorohydrate), reduce the formation of perspiration.

The use of antimicrobial substances in cosmetic deodorants can reduce the bacterial flora of the skin. In an ideal situation, only the microorganisms which cause the odour should be effectively reduced. The flow of perspiration itself is not influenced as a result, and in ideal circumstances, only microbial decomposition of perspiration is stopped temporarily.

The combination of astringents and antimicrobial active substances in one and the same composition is also common.

All active ingredients common for deodorants or antiperspirants can advantageously be used, for example odour concealers, such as customary perfume constituents, odour absorbers, for example the phyllosilicates described in Laid-open Patent Specification DE 40 09 347, of these in particular montmorillonite, kaolinite, illite, beidellite, nontronite,

saponite, hectorite, bentonite, smectite, and also, for example, zinc salts of ricinoleic acid. Antibacterial agents are also suitable to be incorporated into the novel W/O emulsion sticks. Advantageous substances are, for example, 2,4,4'-trichloro-2'-hydroxy diphenyl ether (Irgasan), 1,6-di(4-chlorophenylbiguanido)hexane (chlorhexidine), 3,4,4'-trichlorocarbanilide, quaternary ammonium compounds, oil of cloves, mint oil, thyme oil, triethyl citrate, farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol) and also the active ingredients or active ingredient combinations described in the Laid-open Patent Specifications DE-A-37 40 186, DE-A-39 38 140, DE-A-42 04 321, DE-A-42 29 707, DE-A-43 09 372, DE-A-44 11 664, DE-A-195 41 967, DE-A-195 43 695, DE-A-195 43 696, DE-A-195 47 160, DE-A-196 02 108, DE-A-196 02 110, DE-A-196 02 111, DE-A-196 31 003, DE-A-196 31 004 and DE-A-196 34 019, and the Patent Specifications DE-42 29 737, DE-42 37 081, DE-43 24 219, DE-44 29 467, DE-44 23 410 and DE-195 16 705. Sodium hydrogencarbonate can also be used advantageously.

The list of specified active ingredients and active ingredient combinations is of course not intended to be limiting.

The amount of antiperspirant active ingredients or deodorants (one or more compounds) in the preparations is preferably from 0.01 to 30% by weight, particularly preferably from 0.1 to 20% by weight, in particular 1-10% by weight, based on the total weight of the preparation.

The examples below serve to illustrate the present invention without limiting it. The numerical values in the examples are percentages by weight, based on the total weight of the respective preparations.

Examples:

	1	2	3	4	5	6
	W/O	W/O	W/O	O/W	O/W	O/W
Titanium dioxide (Eusolex T2000)	2	4	6	3	5	2
Zinc oxide	5		4			4
Titanium dioxide (Titandioxid T805)			2			
Silica (Aerosil R972)		1	0.5			
Talc (Talkum Micron)		0.5				
Boron nitride		2				
Sodium maize starch n-octenylsuccinate				0.5		1
Hydroxystearyl hydroxystearate (Elfacos C26)	2		2			
C <sub>20-40</sub> -alkyl stearate (Kesterwachs K82)	1	1				2
C <sub>16-38</sub> -alkylhydroxystearoyl stearate (Kesterwachs K80P)		2		3		5
Behenoxy dimethicone (Abil Wax 2440)			5		5	
Polyisobutene (Rewopal PIB 1000)	5					
Caprylic/capric triglyceride	5	5	5	20	20	20
Octyldodecanol	5		5	15		15
Mineral oil	10			10		20
Butylene glycol caprylate/caprate		10	10		20	7
C <sub>12-15</sub> -alkyl benzoate	10	10	10	5	15	
Dimethicone		2	3			
Dicaprylyl ether (Cetiol OE)				5		
Hydrogenated polyisobutene (Polysynlan)	2					
Methylbenzylidene camphor		3			4	
Octyltriazone		1			4	
Dibenzoylmethane		2			2	
Diethylbutamidotriazole (UVASORB HEB)		2				
Preservative	0.5	0.5	0.5	0.5	0.5	0.5

	1 W/O	2 W/O	3 W/O	4 O/W	5 O/W	6 O/W
Glycerol	5	10	3	5	5	5
Biosaccharide gel (Fucogel 1000)			5			
Hyaluronic acid					0.5	
NaCl	1		1			
MgSO <sub>4</sub>		0.5				
Phenylbenzimidazolesulphonic acid		1			2	
Carbomer (Carbopol 981)				0.1		
Xanthan gum				0.3		
Cellulose gum (Natrosol Plus 330 CS)			0.1			
NaOH 45%		0.3		0.1	0.7	
EDTA solution		1			1	
Water	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100